

## Impact of organic matter and speciation on the behaviour of uranium in submerged ultrafiltration

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### Abstract

*Influence of organic matter (OM) on uranium removal mechanisms by ultrafiltration (UF) over a pH range of 3-11 were investigated. Humic, alginic and tannic acid were used as OM. It was found that uranium adsorbed strongly to the membrane while retention by size exclusion did not occur. Adsorption was dependent on pH and type of OM used. Speciation predictions performed using visual Minteq explain some of these results. In the absence of OM, uranium primarily adsorbed to the membrane at pH 5 and 7 where  $\text{UO}_2\text{OH}^+$  and  $\text{UO}_2\text{CO}_3$  were the dominant species. In the presence of humic acid (HA), uranium adsorption increased from pH 3 (11%) to pH 7 (74%) due to complexation. The structure of alginic acid (AA) did not favour complexation with uranium and therefore did not have a significant influence on its behaviour in UF. The exception was at pH 3 where adsorption increased from 2% to 52%. At this pH no charge repulsion between the uranium species and the AA occurs and complexation is favoured. The highest effect on uranium adsorption was obtained in the presence of tannic acid (TA) at pH 10 and 11 where adsorption increased from 20% up to 100%. Uranium is most likely forming complexes with the gallic acid fraction of the dissociated TA.*

**Keywords:** Uranium, Ultrafiltration, Organic Matter, Uranium-organic matter complexation, Adsorption

## 1. Introduction

Uranium occurs naturally in the environment, both in geology and in water. Generally it is found in ground water at concentrations below 15 µg/L, which is the WHO drinking water guideline [1]. Higher levels in ground and surface waters up to 1 mg/L [2] can, however, be found both naturally and due to anthropogenic activities such as mining and milling of uranium and other minerals [3]. High uranium concentrations are considered a health concern due to the natural radioactivity of the element and its chemical toxicity, which may cause damage to the kidneys and also accumulate in bone [4]. Uranium must therefore be removed from possible drinking water sources.

Uranium has a range of oxidation states of which +IV (uranous) and +VI (uranyl) are the most important [5]. In oxidising conditions uranium tends to be present as the uranyl ion ( $\text{UO}_2^{2+}$ ) [6]. The pH range of natural waters has been found to vary from pH 2 (*e.g.* for acidic mine waters) up to pH 11 (for saline waters) [5] and depending on the pH,  $\text{UO}_2^{2+}$  forms strong complexes with different ligands. Important ligands include carbonates [7, 8] and natural organic matter [9] and the dominating complexes formed will determine uranium behaviour. A variety of investigations explore possible structures of uranium complexed with different types of OM [10], though unfortunately these studies only focus on the lower end of the acidic pH range [11, 12].

Due to the low operating energy required compared to nanofiltration and reverse osmosis, ultrafiltration (UF) is an attractive process for water treatment [13]. It has been shown that complexed uranium can be removed by UF with high retentions reported [14, 15]. Considering that OM can be retained by UF to some extent [13] and influences the retention of metal ions [16, 17], an investigation into the removal of uranium-OM complexes by UF would therefore be valuable. For the purpose of this study three types of OM, representative of compounds found in natural waters, were chosen as suitable for further exploration: HA, AA and TA. HA accounts for a large portion of the natural OM extracted from rivers and streams [18]. AA was chosen as a representative of polysaccharides present in natural waters (*e.g.* as brown algae [19, 20]) and wastewater effluents [21]. AA is known to be highly effective in the removal of metals from aqueous solutions [19, 20, 22], including uranium adsorption in waste water treatment [23, 24]. In fact the combination of AA with membrane processes has been found to lead to enhanced metal removal [16, 17]. TA is a representative of plant polyphenols. Vegetable tannins are plant metabolites readily present in trees [25] and thus found in natural waters. TA is used as a nucleation agent in textiles where it adsorbs/diffuses into the textile and then reduces the metals added, thereby attaching these to the textile structure [26].

The aim of this study was to investigate the influence of OM on uranium removal by UF across the pH range. This illustrated the influence of uranium speciation and complexation with OM on retention mechanisms.

## 2. Materials and Methods

### 2.1. UF membrane and set-up

A schematic of the UF system used is shown in Figure 1. A GE Zenon ZeeWeed hollow fibre module (ZW1) was used in all the experiments. The nominal pore size of the membrane was 0.04 µm and the membrane surface area was 0.047 m<sup>2</sup>. The membrane material is polyvinylidene fluoride (PVDF).

[Figure 1]

The module was operated in an “outside-in” configuration, submerged in 2.55 L of magnetically stirred feed solution and permeate was extracted by vacuum (constant flow rate of 50 mL/min) and re-circulated back to the feed container. The peristaltic pump used to withdraw the permeate was a Masterflex Laboratory/Standard L/S with a digital variable-speed console drive with Masterflex Norprene L/S 16 tubing of inner diameter 3.1 mm. Further equipment consisted of pressure transducer (PX219-30V45G5V) and a thermocouple (TJ2-CPSS-M6OU-200-SB) connected to a datalogger (OMB DAQ 54) for data recording (Omega, UK). Conductivity and pH were measured by using a pH/Cond 340i meter (WTW, Germany).

### 2.2. Chemicals and reagents

Four different experimental solutions were made (all containing a background electrolyte solution): 1) uranium without OM, 2) uranium with HA, 3) uranium with TA and 4) uranium with AA. The OM was purchased from Sigma Aldrich UK. A concentration of 25 mgC/L was used. Uranyl nitrate (TAAB, UK) was added to make up 0.5 mg/L uranium solution. The background electrolyte solution consisted of 1 mM  $\text{NaHCO}_3$ , 0.5 mM  $\text{CaCl}_2$  and 10 mM NaCl all of analytical grade (Fisher Scientific, UK). To adjust the pH to the required levels (pH 3 to pH 11), 1 M analytical grade HCl or NaOH were used (Fisher Scientific, UK). Cleaning solutions were made up using 0.5 g/L sodium dodecyl sulfate (SDS) (Sigma Aldrich, UK) and commercial bleach (Sainsbury's, UK).

### 2.3. Organic matter properties

The properties of the OM such as charge, size and functional groups influence uranium complexation. The properties will also influence the OM interaction with the membrane. A general overview of the OM properties is given in Table 1. Important functional groups of HA include carboxylic, phenolic and alcoholic hydroxyls [27]. AA consists of linear polysaccharides containing mannuronic and galuronic acid (M and G, respectively) arranged in a non-regular block-wise order [19]. M and G block sequences ( $F_{MM}$ ,  $F_{GG}$  and  $F_{MG}$ ) display different structures and their proportions in the alginate determine the metal binding capacity. The lower the M/G ratio and the higher the  $F_{GG}$  content in the alginate, the higher the affinity to bind with metal ions [19, 22]. TA is a hydrolysable tannin with a fundamental structure of glucose and gallic acid (GA) [25].

[Table 1]

#### 2.4. Filtration procedure

The feed solution was prepared and pH adjusted 15 to 18 hours prior to the experiment to allow for the uranium and OM to equilibrate. Samples were taken before and after pH equilibration to confirm that there was no adsorption to the beaker. Conductivity, pH, temperature and trans-membrane pressure were monitored hourly during the experiments, which lasted five hours. The first three parameters remained stable throughout the experiment. When pH changes occurred, online pH adjustments were carried out. Permeate and feed samples (15 mL) were collected hourly for inductively-coupled plasma-optical emission spectroscopy ICP-OES (5 mL) and total organic carbon (TOC) analysis (10 mL). Membrane cleaning was conducted at the end of each experiment. The following protocol was used: MilliQ water backwash (15 min) to remove reversible fouling; nitric acid backwash (15 min) at pH<2 to remove uranium; SDS backwash (15 min) to remove OM, followed by a bleach backwash (30 min, 10% v/v) to further remove OM deposited on the membrane surface. AA was more difficult to remove and a NaOH backwash (20 min, 0.02M) was used in addition.

Analysis of the samples collected after the MilliQ water backwash allowed determination of the mass adsorbed corresponding to reversible fouling. The remaining mass adsorbed corresponded to irreversible fouling. Membrane deposition of uranium and OM was quantified by mass balance given by equation (1) and corrected for collected samples:

$$\text{Mass Deposited (\%)} = \frac{V_{F0}C_{F0} - V_{F5}C_{F5} - \sum_{i=0}^{i=5} V_S C_{Fi} - \sum_{i=0}^{i=5} V_S C_{Pi}}{V_{F0}C_{F0}} \times 100 \quad (1)$$

Where  $V_F$  is the feed volume (L),  $C_F$  is the feed concentration (g/L),  $C_P$  is the permeate concentration (g/L),  $V_S$  is the sample volume (L) and  $i$  are the hourly collected samples (from 1 to 5).

#### 2.5. Analytical methods

The samples and blanks for uranium analysis were stored in polypropylene centrifuge tubes (15 mL), acidified with nitric acid (Aristar, VWR International, UK) to pH < 2 and analyzed with ICP-OES (Perkin Elmer Optima 5300 DV, UK). Calibration standards were made using ICP uranium standard solution (Merck, Germany). The calibration was verified using a certified reference material (ICP Multi Element Standard Solution VI CertiPUR, Germany). The stability of the run was controlled by inserting check standards every 10 samples. Samples for TOC determination were kept in capped glass vials (20 mL) at 3-4 °C until they were analyzed. TOC was determined using a TOC analyzer (Shimadzu TOC-V<sub>CPH</sub>, UK) with an ASI autosampler. Analyses were conducted in non-purgeable organic carbon mode (NPOC) used for low concentration samples.

#### 2.6. Solution speciation

Speciation calculations were performed using Visual Minteq 2.53 (KTH, Stockholm, Sweden). Visual Minteq 2.53 which was updated in October 2007, uses the latest major review on thermodynamic data on uranium. This includes a thermodynamic database for uranium and “generic” HA parameters [28]. Based on the ion composition of the experimental solutions, the speciation was calculated for each pH. The dominant species predicted for each pH were then selected for a “sweep test” performed from pH 3-11, at incremental steps of 0.5. The CO<sub>2</sub> was set to atmospheric pressure (3.9 10<sup>-4</sup> bar) and temperature to 25°C. For HA speciation, the Stockholm Humic Model (SHM) and NICA-Donnan

model were both tested and compared to the experimental data. They both predicted HA to dominate the speciation at acidic to neutral pH (also found by [29]). Based on the correspondence with the experimental results the SHM model was chosen.

### 3. Results and Discussions

#### 3.1. Uranium retention

The filtration of uranium over the pH range 3-11 was investigated as speciation affects the characteristics of uranium, the ligand formation between OM and uranium and the interactions between membrane and uranium species. This might affect retention by UF. However, uranium was not retained by the UF membrane (see Figure 2 A) due to the size of uranium species (UO<sub>2</sub><sup>2+</sup>), which are much smaller (~1.8 Å) [30] than the 0.04 µm (400 Å) membrane pore size.

[Figure 2]

The uranium complexes formed with TA and HA were also not retained (see Figure 2 B and D) and were thus smaller than the membrane pore size. An exception was with AA where a difference was observed between the final feed and permeate concentration of uranium (see Figure 2 C) and AA (not shown). Although AA was not expected to be retained based on its molecular radius of 16.2 nm [31], the final retention of AA ranged from 50 to 80% (data not shown) over the pH range studied. Retention of AA severely affected membrane performance, which indicated high fouling of the membrane (data not shown) as reported by several authors [16, 32, 33]. AA chains can become interconnected promoting gel network formation [19] thus decreasing membrane flux and effective pore size and increasing uranium retention. An important finding of this study was that uranium concentration changed in the feed (and permeate) with time. For example, at pH 5 and 7 (Figure 2 A) uranium feed concentration decreases from 0.5 mg/L to less than 0.1 mg/L at the end of the experiment. This was attributed to membrane deposition or sorption and will be investigated in the following section.

#### 3.2. Uranium deposition on the membrane

It is apparent that 70-80% of the uranium adsorbed to the membrane at pH 5 and 7 (see Figure 3). Uranium deposition on the membrane could be explained by the characteristics of different species formed over the pH range (3-11), namely UO<sub>2</sub><sup>2+</sup>, UO<sub>2</sub>OH<sup>+</sup>, UO<sub>2</sub>CO<sub>3</sub>, Ca<sub>2</sub>UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> and UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup> (see Figure 3). While at pH 3-5, UO<sub>2</sub><sup>2+</sup> is stable in solution, several other studies confirm significant adsorption of uranium around pH 5-7 as UO<sub>2</sub>OH<sup>+</sup> starts to dominate, on a variety of media including natural subsurface media [34], polypropylene, Teflon and polycarbonate containers [35] and silica based materials. The authors explain the sorption mainly through ion exchange of the UO<sub>2</sub>OH<sup>+</sup> species with hydroxyl groups on the surface [36, 37]. Giblin *et al.* [38] confirmed that adsorption occurs more easily for UO<sub>2</sub>OH<sup>+</sup> compared to UO<sub>2</sub><sup>2+</sup>. This was due to surrounding water molecules being less attracted to UO<sub>2</sub>OH<sup>+</sup>, allowing it to react with the surface of the studied material. The log *K* values (stability constants) can also indicate the tendency of a species to remain in solution. UO<sub>2</sub>OH<sup>+</sup> has the lowest log *K* value (-5.25), compared to other species predicted. At pH 7 where adsorption to the membrane prevailed, UO<sub>2</sub>CO<sub>3</sub> was predicted to dominate. This species is highly polar, displaying a net positive charge by the uranium atom [39], and could thus adsorb to the membrane by electrostatic attraction. At pH 8-11 Ca<sub>2</sub>UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> and UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup> dominated. These are generally soluble in water

[3, 5, 40] and therefore no adsorption of uranium was observed at alkaline pH. Although there was adsorption of uranium in the pH range studied this did not appear to affect membrane performance. The uranium species adsorbed were too small to cause any resistance to permeate flux. The possibility of uranium adsorption affecting membrane performance over a prolonged period of time was not investigated however.

[Figure 3]

### 3.3. Influence of organic matter on uranium deposition

As seen in Figure 4 A uranium adsorption was not significantly affected by TA in the acid and neutral pH range as confirmed by Li *et al.* [41] at acidic pH. The more dramatic effect was at pH 10 and 11, where an increase in uranium adsorption from less than 30% up to 100% occurred. This indicated that the presence of TA at high pH had a clear impact on the fate of uranium in the filtration process through complexation between uranium and TA. Similarly, higher adsorption of metals to TA was found by Uçer *et al.* [42] with increasing pH, possibly due to the dissociation of TA.

[Figure 4]

In the present study, a colour change took place during the alkaline pH adjustment of the TA solutions, from a clear solution to a dark green colour. Such colour change at alkaline pH was reported by Makkar and Becker [43], who determined a change in the TA solution without a change in phenolic content. In fact TA is easily degraded by water, acids, bases and certain enzymes to yield glucose and gallic acid [25, 44, 45]. It has been shown that metals attach to the galloyl part of the TA [46], which at high pH dissociates into gallic acid. Gallic acid is known to complex with uranium [47]. Indeed precipitation of uranium from solution using hydrolysable TA at pH 10 [48] has resulted in an adsorption of up to 80% uranium. Yoon *et al.* [49] described a method for uranium removal: TA extract and  $\text{CaCl}_2$  were added at alkaline pH. The solution was sedimented, thereby removing uranium. Despite expecting charge repulsion between the negative uranium species at alkaline pH and the negatively charged gallic acid ( $\text{pK}_a$  in Table 1) the  $\text{Ca}^{2+}$  ions present in the solution could potentially act as a bridge between gallic acid, the ligands on the uranium ion and the membrane.

Results in Figure 4 B show that the presence of AA enhanced adsorption of uranium at  $\text{pH} < 5$ . Under these conditions AA precipitates [20] and forms a gel that is compact due to reduced charge repulsion between the neutral molecules [50]. Since uranium is positive at this pH range (Figure 3), it is likely to form complexes with AA as opposed to more alkaline conditions when both uranium and AA are negatively charged. No enhanced adsorption was obtained at neutral or alkaline pH in the presence of AA. The AA structure determines how well it binds with metals. The affinity increases with G content due to its zig-zag structure which can accommodate the metal ions [19, 20]. This is known as the egg-box model [19, 20, 22]. *Mycrocystis Pylifer* which is the AA species used in this study has one of the highest M/G ratios: 1.6-1.7 [20, 22, 50], thus it is less favourable to metal binding compared to other types of alginates available. Divalent metals have been found to be favoured by AA adsorption [19, 50]. Considering that at pH 3-5 the divalent species  $\text{UO}_2^{2+}$  dominates this explains the high complexation by AA and consequent deposition of uranium. Metal size is also a key variable according to the egg-box model, due to the rigid nature of the GG linkages as well as the steric arrangement of the electronegative ions surrounding the metal.  $\text{Ca}^{2+}$  (1.00 Å) has been found to be selectively favoured by AA over other metal ions [22]. Considering that the smallest species of uranium is found in the form of

$\text{UO}_2^{2+}$  with a radius of 1.8 Å [30] and that at more alkaline conditions the uranium species are even larger (4.85 Å) [51], complexation with AA would be less favoured in the neutral and alkaline pH range.

HA has an ability to interact with metal ions [27] as it contains voids which can trap and retain other components [27]. Carboxyl [52] and phenolic groups [53] present in HA have been found to be important for uranium-HA complexation. In the pH range 3-7, HA had a higher deposition compared to alkaline pH (Figure 4 C). At low pH, HA is by definition insoluble [18, 54] and has a more compact configuration due to the reduced charge density (see Table 1) at both inter and intramolecular levels [55]. Using Visual Minteq, the complexation of uranium with HA was predicted to be dominated by HA between pH 3-7 (Figure 5), at which stage stable water soluble carbonate complexes become important. These speciation results confirmed experimental results where HA increased adsorption of uranium at pH 3-7 (Figure 4 C and Figure 5). This also confirmed results from a variety of studies where HA has been found to be important in uranium complexation in the acidic and neutral pH range and increase uranium adsorption onto different materials [56, 57]. Li *et al.* [41] also found that uranium-HA complexation was important at low pH. They determined that the uranyl ions in solution decreased at pH 5, but did not study uranium without OM to confirm whether or not this was due to the OM.

[Figure 5]

This study clearly shows the significant effect of the different types of OM in uranium removal by UF. Solution characteristics such as pH and presence of  $\text{Ca}^{2+}$  determined whether complexation was favoured, enhancing adsorption of these complexes on the membrane.

## 4. Conclusions

The fate of uranium in the UF process was highly dependent on solution characteristics such as pH and type of OM. With the exception of AA, retention by size exclusion was not observed irrespective of the presence of OM. A significant amount of adsorption of uranium and uranium-OM complexes on the membrane was observed at certain conditions, for example at pH 5 and 7 in the absence of OM. Stronger adsorption was observed when the uranium solution was filtered in presence of HA at pH 3 to 7, where according to speciation calculations, uranium formed complexes with the HA. The presence of AA did not affect uranium deposition significantly since the chosen alginate did not possess the necessary characteristics to bind metals. The adsorption of uranium was highest (75-100%, 18.4 - 24.4  $\text{mg/m}^2$ ) in presence of TA at pH 10 and 11 where uranium was postulated to complex with gallic acid, originating from the dissociation of TA. Speciation calculation of uranium with HA was a useful tool to understand the results that were obtained in regards to the behaviour of uranium in the UF process. Current limitations are the availability of a variety of organic molecules in such databases.

Significant findings from this study highlight that through simple adjustments to the water such as pH control and/or addition of complex forming molecules such as OM, uranium may be removed using UF. This process can be used as pre-treatment of NF/RO, where removal of these complexes by UF may help prevent scaling and organic fouling of the tighter membranes. Removal of metals such as uranium from industrial effluents (such as mining), uranyl in nuclear decommissioning related effluents or contaminated water supplies are applications where the influence of solution chemistry and OM are important. Further studies investigating the impact of co-precipitation on uranium removal by membrane filtration are warranted.

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## 6. References

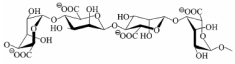
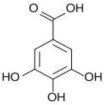
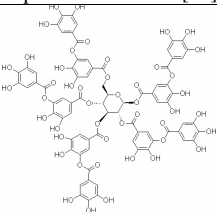
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Table 1 Organic matter properties

Compound	Molecular Structure	Molecular Weight (g/mol)	pKa ( - )
Alginic Acid		12,000-80,000 [50]	3.44 [19, 20]
Gallic Acid		170	3.13-9.2 [58, 59]
Humic Acid	Proposed structure in [60]	1000 - >300,000 [61]	3.5 - 5.04 [61]
Tannic Acid		1701	-

List of figures

Figure 1 Ultrafiltration submerged system (P: pressure transducer, T: thermocouple)

Figure 2 Uranium final feed and permeate concentration with different OM types (at t=5 h). A) without OM, B) TA, C) AA and D) HA. Feed solution: 0.5 mgU/L as  $\text{UO}_2(\text{NO}_3)_2$ , 1mM  $\text{NaHCO}_3$ , 0.5 mM  $\text{CaCl}_2$ , 10 mM  $\text{NaCl}$ , 25 mgC/L OM. All error bars represent the relative error calculated from three repeat experiments.

Figure 3 Uranium membrane deposit (at t=5h) and uranium speciation in absence of OM as a function of pH. Feed solution: 0.5 mgU/L as  $\text{UO}_2(\text{NO}_3)_2$ , 1mM  $\text{NaHCO}_3$ , 0.5 mM  $\text{CaCl}_2$ , 10 mM  $\text{NaCl}$ .

Figure 4 Uranium and organic matter membrane deposit (at t=5h) for A) TA, B) AA and C) HA. Feed solution: 0.5 mgU/L as  $\text{UO}_2(\text{NO}_3)_2$ , 1mM  $\text{NaHCO}_3$ , 0.5 mM  $\text{CaCl}_2$ , 10 mM  $\text{NaCl}$ , 25 mgC/L OM.

Figure 5 Uranium membrane deposit (at t=5h) and speciation of uranium-HA solution as a function of pH. The solution speciated was 0.5 mgU/L as  $\text{UO}_2(\text{NO}_3)_2$ , 1mM  $\text{NaHCO}_3$ , 0.5 mM  $\text{CaCl}_2$ , 10 mM  $\text{NaCl}$ , 25 mgC/L HA (HA from the Minteq data base).

Figure 1

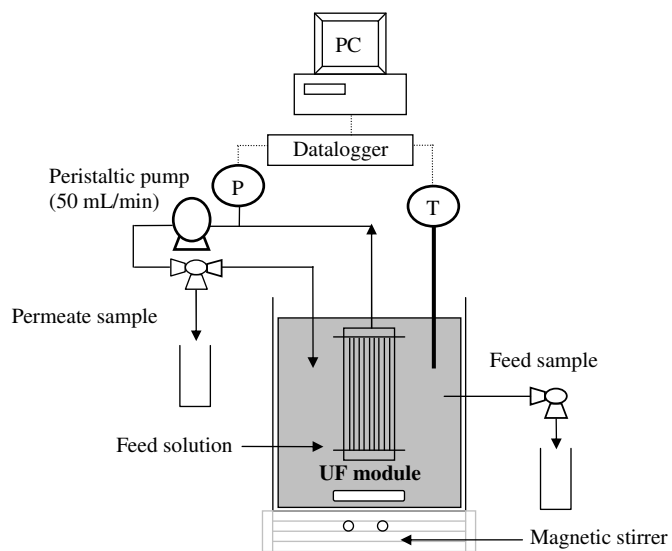


Figure 2

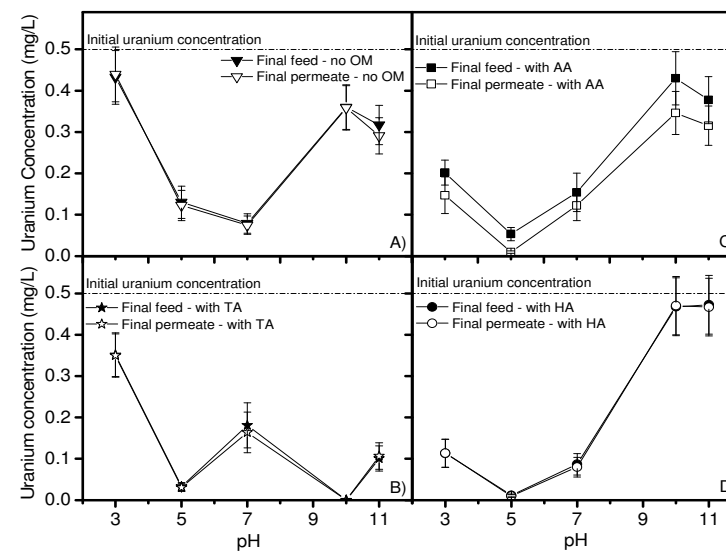




Figure 3

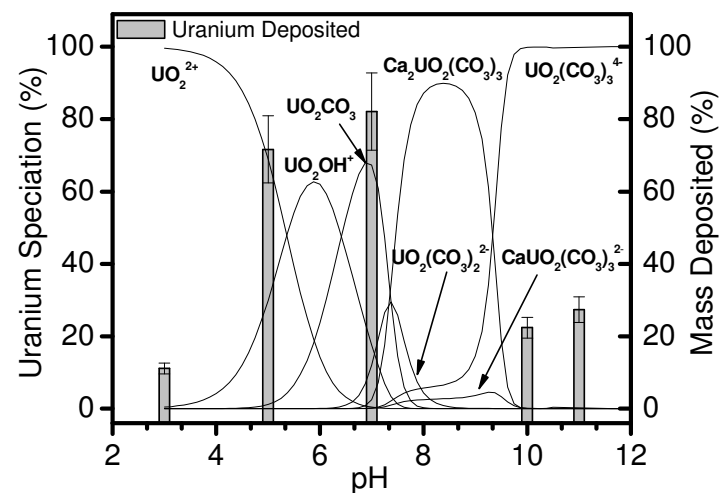


Figure 4

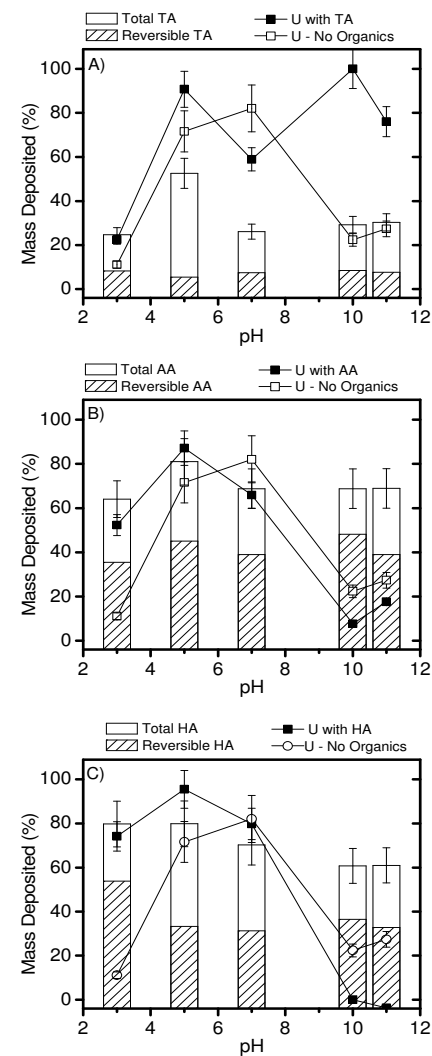


Figure 5

